AD NUMBER
ADA800405
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AUTHORITY
E.O. 10501 dtd 5 Nov 1953; NAVSEA ltr dtd 4 Dec 1968

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Bausch and Lomb Optical Co., Rochester, N.Y.

Interim Research Report for Radiophotoluminescent and Tenebrescent Glasses - 24 Oct to 24 Nov 1951

Kreidl, N.J. 24 Nov'51 18pp. graphs

USN Contr. No. NObsr-57016

Glass - Optical properties
Luminescence
Crystals - Growth
Gamma rays

Materials, Non-Metallic (8)
Ceramics (1)

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Report Number _____ Date 24 Oct. 1951 to 24 Nov. 1951

Subject INTERIM RESEARCH REPORT

FOR

RADIOPHOTOLUMINESCENT AND TENEBRESCENT GLASSES

NAVY DEPARTMENT BUREAU OF SHIPS ELECTRONICS DIVISIONS

NObsr-57016 NE-051551

By N. J. Kreidl

Chemical Research Director

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Rochester 2, New York

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INTERIM RESEARCH REPORT

FOR

RADIOPHOTOLUMINESCENT AND TENEBRESCENT GLASSES

This report covers the period 24 October, 1951 to 24 November, 1951

BAUSCH AND LOMB OPTICAL CO.

ROCHESTER 2, NEW YORK

NAVY DEPARTMENT BUREAU OF SHIPS ELECTRONIC DIVISIONS

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ABSTRACT

Contractual Matters

All necessary equipment and consultation approvals have been applied for and delivery dates scheduled. Authority required for purchase of radioactive material has been received from the Atomic Energy Commission.

Tenebrescence

K_2O was found as one of the fundamental factors in the sensitivity of tenebrescent glasses, as one of the results of a study of the systems K_2O-Al_2O_3-P_2O_5 and BaO-Al_2O_3-P_2O_5.

A theoretical study on tenebrescence was initiated and a program of experiments derived from preliminary results.

Calibration Glasses for Radiophotoluminescence

Glasses containing Mn^{++} have been found which essentially duplicate the photoluminescence of the radiophotoluminescent glass.

Radiophotoluminescence

The addition of small amounts of certain modifiers did not improve the working properties of the existing radiophotoluminescent glass.

1. # PART I

PRESENT STATUS

1.1 PURPOSE

The purpose of this investigation is to determine, in glasses, the causes of optical changes produced by X - or gamma radiation, to select and develop these compositions which combine optimum indication and integration of X or gamma radiation with desirable technological properties affecting their eventual manufacture, and to develop a glass which without radiation by X or gamma rays will fluoresce in a manner similar to the existing dosimeter glass.

1.2 GENERAL FACTUAL DATA

1.2.1 Personnel

Since the report of 24 October, 1951 the project has lost the services of G. Sherwood Smith (indicated in a special report) who was ordered to active duty on 2 November, 1951 as a 2nd Lieutenant, CE, U.S.A.R.

The Iowa Military District, Building 92, Gruber Street, Des Moines, Iowa turned down the request for deferment submitted by this company to the New York Military District on 30 October, 1951.

This company will appeal the decision on the basis that four years training in Ceramics is a scarce commodity. Coupled with Mr. Smith's work on this project, it represents a more extensive and more critical investment than his ROTC training.

In order to prevent delay in the project, Mr. G. Brewster was shifted from a purely advisory capacity to carrying on the melting operations. This company's projects have been put on an overtime basis to allow this project to operate during normal working hours. This was reported to Bureau of Ships, via Naval Inspector of Ordnance in a letter dated 23 November, 1951.

Authority to utilize the services of Dr. K. H. Sun, Pittsburgh, Pennsylvania, to cooperate with Dr. Kreidl, of this project, in writing a survey of the scientific background as a basis for the investigations

of this contract was requested by letter dated 10 October, 1951 to the Contracting Officer, Bureau of Ships. This has not yet been authorized.

1.2.2. Equipment and Facilities

Authority to purchase the necessary source of gamma radiation, equipment for its safe handling, and the monitoring equipment required by the Atomic Energy Commission was requested on 18 October, 1951. This authorization has not been received. Our authority from the Atomic Energy Commission to purchase radiocobalt expires 31 December, 1951. Delivery dates on our equipment orders have been quoted by our supplier, on some items involved, as 90 days.

Authority to erect 13 feet of wall to separate the radiocobalt source from the rest of the laboratory in compliance with general requirements of the Atomic Energy Commission, was requested 12 November, 1951. This request has not been authorized.

The gradient furnace, mentioned later, is one which this laboratory constructed from ideas gained from the paper "An Improved Apparatus for the Determination of Liquidus Temperature and Rates of Crystal Growth" by O. H. Grauer and E. H. Hamilton of the National Bureau of Standards (Journal of National Bureau of Standards 44 (1950) R.P. 2096).

1.3 DETAIL FACTUAL DATA

1.3.1 Topic I - Radiophotoluminescent Glasses

(Note: Topic I has been generalized from title used in first report)

(Note: Topic I is temporarily emphasized as it does not in its initial phase require testing equipment not yet available.)

1.3.1.1 Devitrification

1.3.1.1.1 Purpose

The purpose of this phase of the work was to find modifications of composition which had less tendency to devitrify (grow crystals) when made in larger crucibles than are used in the laboratory, and which had a longer working range (rate of change of viscosity with temperature is less).

1.3.1.1.2 Experimental Approach

The approach to this problem was to modify the r-glass by small amounts of MgO, Al_2O_3, ZnO, or SiO_2.

The following compositions were melted:

Melt No.	$Al(PO_3)_3$	KPO_3	$Ba(PO_3)_2$	$Mg(PO_3)_2$	$Zn(PO_3)_2$	Al_2O_3	SiO_2
1A-3707	50.0	25.0	20.0	2.00	2.00	1.00	-
1A-3708	50.0	25.0	19.0	2.00	2.00	1.00	1.00

All compositions are weight percent.

These glasses were compared with r-glass in the gradient furnace, to determine devitrification tendencies.

1.3.1.1.3 Results

All glasses were completely devitrified at all temperatures investigated, 500° to 900° C.

1.3.1.1.4 Conclusions

The composition variations showed no improvement in properties. Work will be resumed after making exploratory experiments on other approaches.

1.3.1.2 Phosphate Base

1.3.1.2.1 Purpose

The purpose of this phase of the work was to investigate suitability for radiophotoluminescence of bases chemically related to present base of r-glass but known to have better working properties.

1.3.1.2.2 Experimental Approach

The following composition was melted:

Melt No.	SiO_2	Na_2O	Al_2O_3	B_2O_3	P_2O_5
1A-3709	20.0	20.0	30.0	10.0	20.0

Composition Wt. %

1.3.1.2.3 Results

The melting properties were not good under the conditions tested. Other melting conditions will be studied. The silver solubility of this glass has not been tested.

1.3.2 Topic 2 - Standard Glasses

(Note: Topic 2 is also emphasized because special equipment is not required.)

1.3.2.1 Purpose

The purpose of this work was to develop a glass having the same fluorescence as r-glass without previous irradiation by gamma rays.

1.3.2.2 Background

1.3.2.2.1 A glass, E-9272 having the composition SiO_2-34.1%, Na_2O-23.3%, B_2O_3-33.0%, MnO_2-2.50%, Sb_2O_3-5.65, and As_2O_3-1.50%, developed by this company prior to this study, had been found to fluoresce similarly but much brighter than r-glass.

1.3.2.2.2 The variation of the activator system MnO-Sb_2O_3 to obtain a desired intensity was considered possible, but complicated because of the opposing influences of quenching, oxidation, and color. The quenching phenomena is the reducing of the amount of fluorescence by too much Mn^{++}, the oxidation phenomena is the effect of the ratio of Mn^{++} to Mn^{++} and Mn^{+++} in determining fluorescence, and the color phenomena is the increase in color due the increase of Mn^{+++} which produces an intense purple color causing fluorescence to be affected by thickness. It was considered promising to cut down on the fluorescence of the Mn^{++} by adding a small amount of iron.

1.3.2.3 Experimental Approach

To a glass of the composition of E-9272 substitutions of Fe_2O_3 were made for SiO_2. These are shown below together with a visual estimate of their fluorescence.

Melt No.	Fe_2O_3 Added	Visual Estimate of Fluorescence
E-9530	0.315 Wt. %	Too Dark
E-9541	0.160	Correct
E-9535	0.080	Nearly Correct-but bright

These glasses will be tested by Dr. Schulman at the Naval Research Laboratory. All three glasses have slight brown color.

1.3.3 Topic 3 - Tenebrescent Glasses

1.3.3.1 System Al_2O_3-K_2O-P_2O_5

1.3.3.1.1. Purpose

The Naval Research Laboratory has discovered that r-glass from which silver phosphate is omitted (in the following called r-base) represents one of the best tenebrescent compositions to date. The r-base is a composition in the quaternary system Al_2O_3-K_2O-P_2O_5-BaO. In order to better understand this fact simpler binary and ternary compositions were considered. The theoretical work of N. Kreidl and K. Sun, that will be presented in the next report, suggests attention to the role of K_2O.

1.3.3.1.2 Experimental Approach

Melts were made of various compositions in 2 inch zircon crucibles.

1.3.3.1.3 Results

1.3.3.1.3.1 The approximate glass formation area in this system is indicated by the solid line in the composition field of figure 1. Glasses to the right of the dashed line were not investigated. Such glasses, containing more P_2O_5 than the metaphosphates, are usually soluble in water, difficult to prepare, and unreliable in composition due to the volatilization of P_2O_5. However, glass formation is expected to exist in most of this area. Glasses produced near the K_2O-P_2O_5 binary side of the field are hygroscopic resulting in poor samples. However, these are of sufficient interest to warrant further attempts to prepare better samples, preserving them in a desiccator.

1.3.3.1.3.2 Since no radiation source was available here, selected samples were prepared and submitted to Dr. Schulman, Navy Research Laboratory, for exploratory examination. Ratings so obtained are inscribed in figure 1. The rating most refers, according to Dr. Schulman, to tenebrescence comparable with the r-base. These results are also shown with the compositions:

Glass	K_2O	Al_2O_3	P_2O_5	Sensitivity
F-0008-1	55	20	25	Slightly less sensitive than 2 and 3
F-0008-2	45	10	45	One of most sensitive
F-0008-3	45	20	35	One of most sensitive
F-0008-4	15	20	65	Slightly more sensitive than 5
F-0008-5	5	30	65	Least sensitive
F-0008-6	35	30	35	Slightly less sensitive than 2 and 3

Compositions are mol %

r-base sensitivity about same as F-0008-2 and 3.

Additional melts as shown have been submitted to Dr. Schulman. These have the following compositions:

Glass	K_2O	Al_2O_3	P_2O_5
F-0008-7	42.5	4.0	53.5
F-0008-8	57.5	2.5	40.0
F-0008-9	37.0	16.0	47.0

Compositions are mol %

The first two glasses were prepared to investigate the field in the absence of alumina, the last glass was a composition between the compositions of F-0008-2 and F-0008-3, the two best of the previous study.

1.3.3.1.4 Conclusions

The results indicate a strong sensitizing influence of K_2O.

1.3.3.2 System Al_2O_3-BaO-P_2O_5

1.3.3.2.1 Purpose

The purpose of this work was to separate the influence of BaO on the sensitivity from the quaternary system (Al_2O_3-BaO-K_2O-P_2O_5) r-base.

1.3.3.2.2 Experimental Approach

Melts were made in the same manner as in 1.3.3.1.2. Samples have been submitted to Dr. Schulman for irradiation.

1.3.3.2.3 Results

1.3.3.2.3.1 Glass formation is indicated as sub A in figure 2.

1.3.3.2.3.2 Radiation results are not yet available.

1.4 CONCLUSIONS

1.4.1 Topic I

1.4.1.1 Devitrification of r-glass cannot be sufficiently prevented with the addition of $Zn(PO_3)_2$, $Mg(PO_3)_2$, Al_2O_3 and SiO_2 for $Ba(PO_3)_2$.

1.4.1.2 Other Base Glasses

No conclusions can be drawn.

1.4.2 Topic 2

The fluorescence of a Mn^{++} glass can be controlled to make it match that of r-glass by adding Fe_2O_3.

1.4.3 Topic 3

1.4.3.1 The K_2O in the π-base is believed to be one of the dominating components in this glass. The domain of usable glasses has been determined for the system K_2O-Al_2O_3-P_2O_5.

1.4.3.2 The domain of usable glasses has been determined for the system BaO-Al_2O_3-P_2O_5.

2. PART II

PROGRAM FOR NEXT INTERVAL

2.1 THEORY

The theoretical study by N. Kreidl and K. Sun will be continued in the hope that it can be submitted in the next interim report.

2.2 EXPERIMENTAL

2.2.1 Topic I

Silver solubility and devitrification will be studied in various phosphate glasses.

2.2.2 Topic 2

Additional work will depend on test results obtained on standards containing small amounts of iron in conjunction with manganese activators.

2.2.3 Topic 3

Planned work, as derived from completed theoretical studies, comprises:

a) Simple phosphate systems (current).

b) Comparison of K_2O-SiO_2 and K_2O-B_2O_3 system with K_2O-P_2O_5 system.

c) Compositions of aluminates particularly potassium.

d) The addition of F, Cl, I, and S to K_2O-P_2O_5-X systems.

e) Investigation of fluoride glasses.

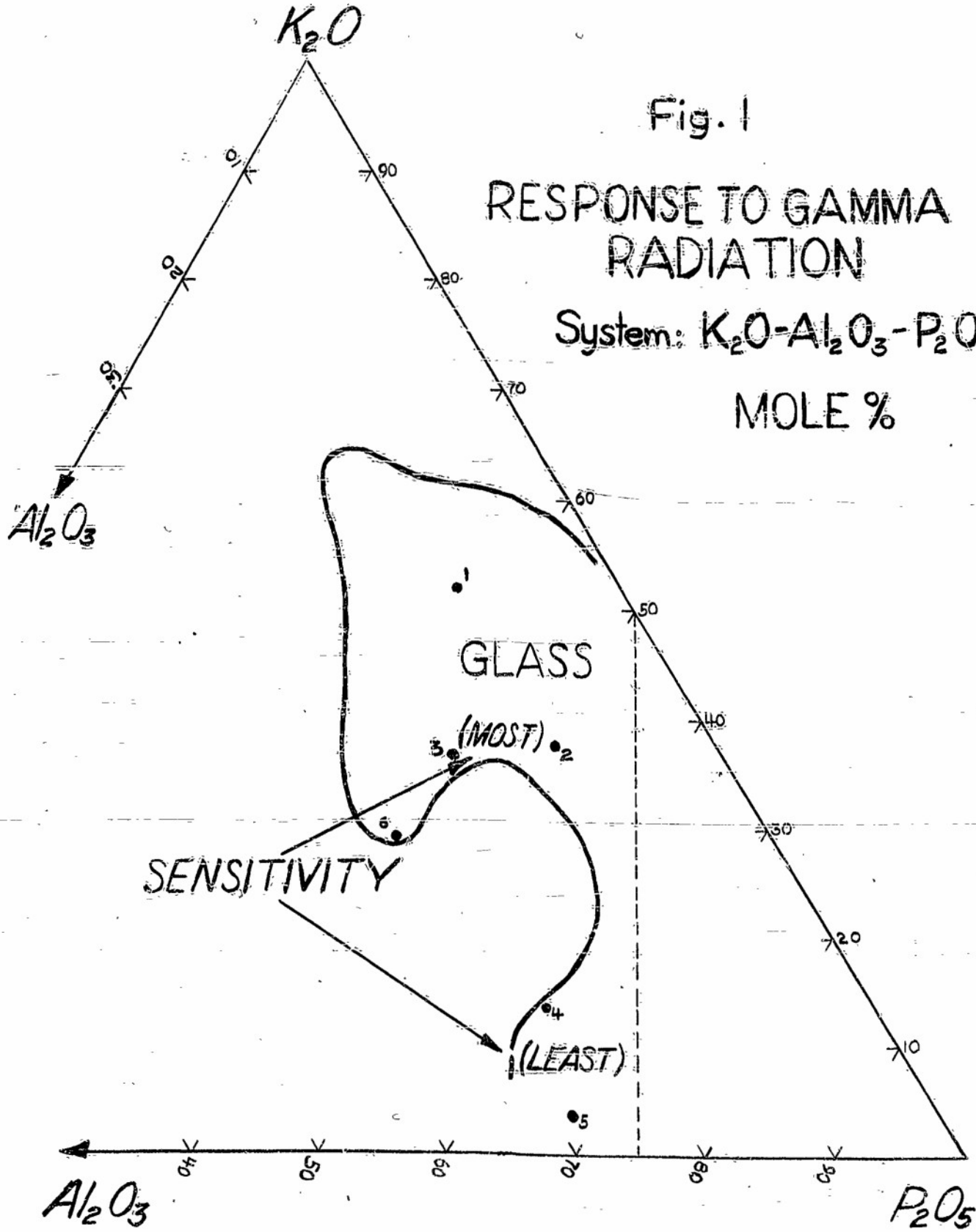

Fig. 1

RESPONSE TO GAMMA RADIATION

System: K_2O-Al_2O_3-P_2O_5

MOLE %

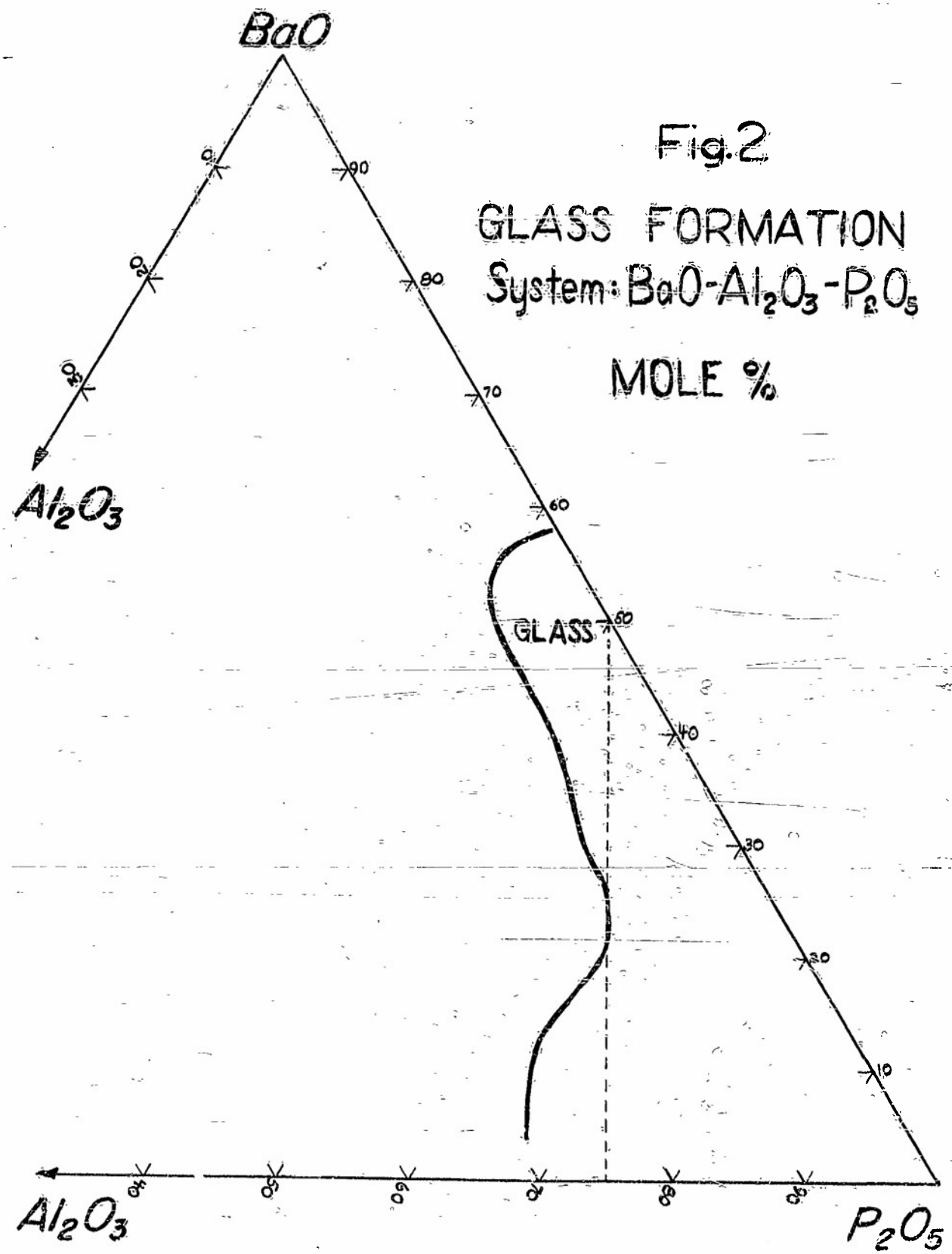

Fig. 2

GLASS FORMATION

System: $BaO-Al_2O_3-P_2O_5$

MOLE %